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FTD-TT- 63-1012

TRANSLATION

OBJECTS FROM URANIUM DIOXIDE

By

P. P. Budnikov, A. S. Berezhnoy et al.

FOREIGN TECHNOLOGY DIVISION

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FTD-TT- 63-1012/1+2

UNEDITED ROUGH DRAFT TRANSLATION

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BY: P. P. Budnikov, A. S. Berezhnoy et al.

English Pages: 7

SOURCE: Tekhnologiya Keramiki i Ogneuporov, Gosstroyizdat, Moscow, (Russian), 1962, 396-399

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FTD-TT- 63-1012/1+2 Date Jan. 9 19 64

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OBJECTS FROM URANIUM DIOXIDE

Uranium is found in nature in form of a crystallinematerial (uraninite mineral) UO_2, which appears to be an important source for obtaining uranium and radium. The chemical composition of the found crystals does not correspond to the mentioned formula; it appears to be an intermediate between UO_2 and UO_2, 67 (U_3O8).

The presence of $U+^6$ in the composition of uraninite, apparently, is due to the process of oxidation. It contains Ra, Ac, Po and other radioactive conversion products. Uraninte is found in granite and syenite pegmatites together with zirconium, tourmaline, monazite, field spar, mica etc. It is often accompanied by minerals, containing rare earth elements, niobium and tantalum. Know are up to 30 minerals - products of oxidation of uranium pitch blende, which contain from 25 to 80% of uranium.

Uranium dioxide represents a dark brownish powdery mineral. The crystalline lattice of UO_2 is cubical face-centered of the fluorite type. Uranium ions in the lattice are situated in angles and on the edges. In fig. 79 is given an elementary oxide cell. Cell dimension (constant lattice) 5,469 Å; the theoretical density calculated by them equals 10, 95 g/cm^2. Index of refraction[1] of UO_2 equals 2355.

Melting point of UO_2 according to Lamberston and Mueller[2] equals $2872+22^\circ$.

When sintering UO_2 the less in weight is noticed already at a temperature of 1400°. But the nature of its volatility has not been established so far.

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1 Johnson R. Fulerson, S. D. Taylor A. J. J. Amer. Ceram Soc. 1957, vol. 36, No. 3, p. 112-117

2 Lamberston W. A; Mueller M. H. J. Amer. Ceram Soc. 1953, vol. 36, No. 10, p. 329

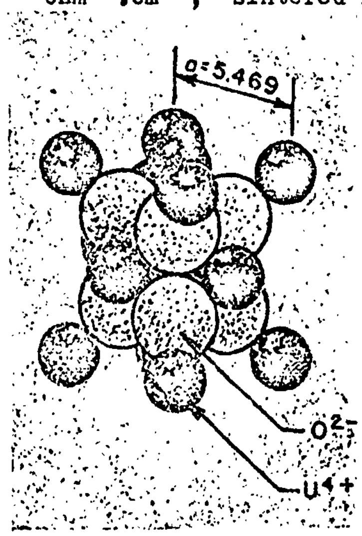
1 According to T. Ehlert and J. Margrace (J. Amer. Ceram. Soc. 1958, vol. 41, No. 8, p. 330) the true melting point of UO_2 $2860 \pm 45^\circ$. Objects from powderous UO_2 can be calcined at 2310°.

Uranium has a series of oxidation stages. In spite of the fact that UO_2 appears to be a stable phase up to the melting point in relativley pure hydrogen, or CO or in vacuo, the effect of oxygen on volatility of UO_2 is considerable even in small quantities.

The heat conduction coefficient of sintered uranium dioxide at its conditionally zero porosity in dependence upon temperature is quite low and equals: at 100° 0.234, at 600° 0.0105; at 1000° 0.00815 cal/cm sec deg. The heat of formation of UO_2 from elements, determined by the burning of uranium in an oxygen current, equals 256 kcal/mol.

Its specific heat at $100^{\circ}K$; Cp=6.958; at 200° 12.47; at 250° 14.17 and at 300° 15.38 cal/mol degr. The elasticity modulus at 20° $17,5.10^{3}$ kg/mm^2.

UO_2 appears to be a semicondutor; its electroconduction depends to a large extent upon the purity and volumetric weight. Specific electro conduction of a rod made of UO_2, obtained by sintering in a hydrogen medium, at room temperature equals 4.10^{-8} ohm^{-1}.cm^{-1}; sintered in nitrogen $3^{\circ}.10^{-5}$ohm^{-1} cm^{-1}.



GRAPHIC NOT REPRODUCIBLE

Figure 79. Elementary UO_2 cell

In comparision with other ceramic materials thermal expansion of UO_2 is relatively great; with a rise in temperature it rises somewhat.

Uranium dioxide possesses highly basic properties. There are data about

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the existence of the following oxides: UO_2, U_4O_9, U_3O_7, U_2O_5, U_3O_8 and UO_3. When exposed to air UO_2 oxidizes at room temperature. So far there are no data about the compositions of the forming oxides.

The structural diagram of the U-O system, constructed by Ackerman on the basis of investigation results of various authors, is given in fig. 80. UO_2 absorbs in its structure oxygen to a composition $UO_{2.30}$ with compression of the elementary cell at this composition to a minimum value of 5.430 Å.

Water with a temperature of up to 300° does not react with UO_2. Physical properties of sintered or pressed uranium dioxide also remain unchanged when heating in an autoclave to indicated temperature. UO_2 does not dissolve in hydrochloric acid (with exveption of fumic), but is soluble in nitric, aqua regia and in a mixture of nitric and hydrofluoric acid. It reacts with HF forming $UF_4 \cdot UO_2$, eoes not react with NaOH, but sodium peroxide dissolves it with formation of Na_2UO_4.

In finely dispersed state uranium dioxide reacts with carbon at 1800°; in the process of calcining at 2300° in the reaction products is detected UC_2 and U_2C_3. With hydrogen UC_2 does not react to the melting point of the oxide. UO_2 does not react with al_2O_3, MgO and BeO up to 1800°. Uranium dioxide forms solid solutions with ThO_2 and ZrO_2. With CaO uranium dioxide forms $CaO.UO_2$ componds and acquires in soldi solution up to ~ 40% mol. CaO.

Up to a temperature of 1800° UO_2 does not react with Si, but a temperatures of 1900 - 2100° it forms USi_2 type silicides. With aluminum UO_2 reacts already at a temperature of 500° with the formation of ULI_4 and UAI_3. With niobium UO_2 reacts with the formation of a solid (Nb-U) a solution and indefinite phase.

Fig. 80 on page 3a

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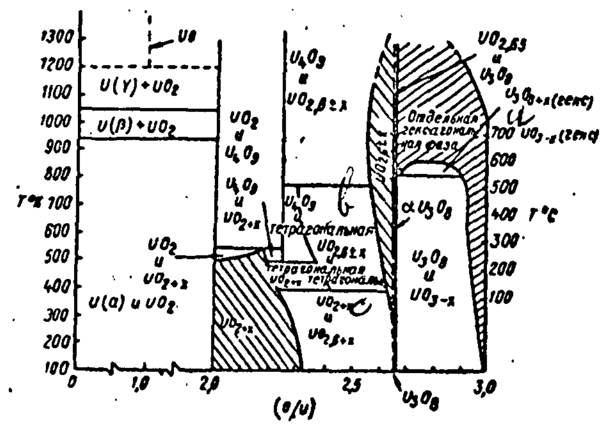

Figure 80. Structural diagram of U-O* system; a-individual hexagonal phase; b-tragonal; c-tetragonal UO_2 tetragonal.

* Additions to U-O diagram see P. P. Budnikov; S. G. Tresvyatskiy; V. I. Kushakovskiy, Doklady Akademii Nauk SSSR, vol. 128, No. 1. 1959, pp 85-88.

Finely dispersed UO_2 has pyrophoric properties, it burns to U_3O_8. It rapidly absorbs oxygen from the air at stabilizes at a composition $UO_{2.15}$.

When heated in air at 600° UO_2 transforms into U_3O_8 and that is why the use of object made from UO_2 is possible only in a neutral or reduced medium.

Highly consitent UO_2 can be obtained by melting in an electric arc followed by pulverization and granulation. Ordinarily UO_2 is subjected to sintering in a hydrogen medium or in an inert gas.

UO_2 appears to be a nonplastic material. Objects made from it can be obtained in various form (crucibles, pipes, cylinders, rods etc), by ordinary technological methods: pressing, dress casting, drawing and hot pressing.

For pressing crucibles is used pulverized chemically pure uranium dioxide. The mass with a moisture of 6-8% is stuffed into a steel chrome plated form. Stuffing of mass into form the purpose of avoiding contamination is done with a uranium rod. Crucibles are pressed in reverse state at pressures of 1200-3000 kg/cm^2. Pressed crucibles are very brittle and special care must be exercised in the handling of same.

Objects can be obtained by pressing an UO_2 powder in steel chrome plated forms under a pressure of 700 kg/cm^2 and by using in role of binder dextrose, wax and other gluing substances. To cast thin walled objects in gypsum forms UO_2 is pulverized in a steel grinder to particles with a dimension of less than 0.06mm.

After removing from the UO_2 powder the iron impurities by processing in HCl and flushing with distilled water the obtained dross should have a pH=2.

Rods and pipes can be formed from UO_2 by drawing the mass on organic plasticizers through steel forms.

Shaped objects are calcined in furnaces with amolybdenum coil at a temp-

erature of 1750° with 2-hours exposure. In the role of base can be used alumina refractories with a coverage of a thin layer of metallic molybdenum. Calcination of items at a temperature of 2000-2200° is realized in vacuum or in an argon medium.

Uranium dioxide, which appears to be a highly fire resistant material and quite stable against corrosion in various media, can be used in atomic reactors in role of fuel in form of granules and massive objects. Granulated UO_2 can be introduced into a mixture of other materials, from which heat separating elements can be manufactured. These mixtures can be used as raw material for the obtainment of secondary nuclear fuel. Fuel rods should be enclosed in zirconium shells.

Uranium dioxide is used for the preparation of crucibles, protective tubes for the mocouples and so on.

When handling UO_2 it is necessary to wear protective gas masks and rubber gloves and to exercise maximum care as result of considerable toxicity for the organism by inhaling radioactive dust or by falling of same on open wounds.

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